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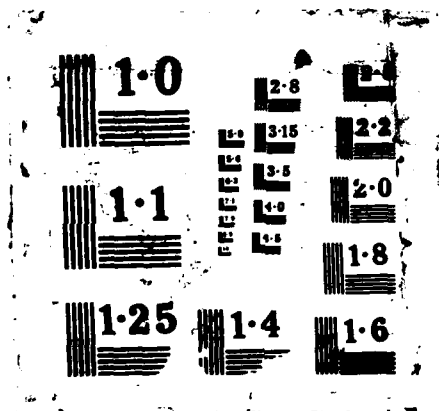
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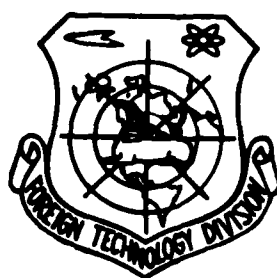
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HIGH-MOLECULAR COMPOUNDS  
(Selected Articles)



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# PARTIALLY EDITED MACHINE TRANSLATION

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4 September 1987

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PREPARED BY:

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Example:

Translation # FTD-ID(RS)T-0204-86 (Provided by SIT)

Foreign Page # \_\_\_\_\_

Incorrect word/phrase: \_\_\_\_\_

Recommendation: \_\_\_\_\_

Foreign page numbers occur in the English text and may be found anywhere along the left margin of the page as in this example:

In them occurs the state named "night blindness" - hemeralopia, which, according to the current point of view, is a result of damage of the rod-shaped apparatus of the eye.

Page 51.

However, in recent years it has been shown that with the hereditary pigment degenerations in animals the biochemical changes are observed in all cellular elements of the retina.

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# U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
А а	<i>А а</i>	A, a	Р р	<i>Р р</i>	R, r
Б б	<i>Б б</i>	B, b	С с	<i>С с</i>	S, s
В в	<i>В в</i>	V, v	Т т	<i>Т т</i>	T, t
Г г	<i>Г г</i>	G, g	У у	<i>У у</i>	U, u
Д д	<i>Д д</i>	D, d	Ф ф	<i>Ф ф</i>	F, f
Е е	<i>Е е</i>	Ye, ye; E, e*	Х х	<i>Х х</i>	Kh, kh
Ж ж	<i>Ж ж</i>	Zh, zh	Ц ц	<i>Ц ц</i>	Ts, ts
З э	<i>З э</i>	Z, z	Ч ч	<i>Ч ч</i>	Ch, ch
И и	<i>И и</i>	I, i	Ш ш	<i>Ш ш</i>	Sh, sh
Й й	<i>Й й</i>	Y, y	Щ щ	<i>Щ щ</i>	Shch, shch
К к	<i>К к</i>	K, k	Ъ ъ	<i>Ъ ъ</i>	"
Л л	<i>Л л</i>	L, l	Ы ы	<i>Ы ы</i>	Y, y
М м	<i>М м</i>	M, m	Ь ь	<i>Ь ь</i>	'
Н н	<i>Н н</i>	N, n	Э э	<i>Э э</i>	E, e
О о	<i>О о</i>	O, o	Ю ю	<i>Ю ю</i>	Yu, yu
П п	<i>П п</i>	P, p	Я я	<i>Я я</i>	Ya, ya

\*ye initially, after vowels, and after Ъ, Ы; e elsewhere.  
When written as ѣ in Russian, transliterate as yě or ě.

## RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English	Russian	English	Russian	English
sin	sin	sh	sinh	arc sh	$\sinh^{-1}$
cos	cos	ch	cosh	arc ch	$\cosh^{-1}$
tg	tan	th	tanh	arc th	$\tanh^{-1}$
ctg	cot	cth	coth	arc cth	$\coth^{-1}$
sec	sec	sch	sech	arc sch	$\operatorname{sech}^{-1}$
cosec	csc	csch	csch	arc csch	$\operatorname{csch}^{-1}$

### Russian English

rot curl  
lg log

### GRAPHICS DISCLAIMER

All figures, graphics, tables, equations, etc.  
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Page 563.

LONG-LIVED RADICALS DURING THE POLYMERIZATION OF METHYLMETHACRYLATE IN  
THE PRESENCE OF PHOSPHORIC ACID.

Ye. S. Garina, Ye. G. Lagutkina, V. P. Zubov, V. A. Kabanov.

Dear editor

With radical polymerization in homogeneous liquid phase at early stages of transformation lifetime of active centers is usually 1-5 s. We discovered, that during the polymerization of methylethacrylate (MMA) in the presence of orthophosphoric acid at usual temperatures appear the long-lived radicals, which lead process actually by the mechanism of "living chains", moreover system remains quasi-homogeneous.

During investigation of photo-initiated polymerization in systems MMA -  $H_3PO_4$  composition of 1:0.3 and 1:6 at 25° are discovered, that after disconnection of source of UV light reaction does not extinguish, but is continued with constant, somewhat less than light, speed up to virtually complete exhaustion of monomer during 10-20 hours (polymerization without preliminary illumination by UV light does not occur). The minimum degree of transformation, after which it is possible to record the nonextinguishing aftereffect, is equal to ~0.5%. During the investigation of the dependence of the speed of after-light polymerization on the depth of conversion,

achieved/reached during uninterrupted photoinitiation, it seemed that with an increase in the degree of conversion with the illumination the ratio of the velocity of post-polymerization to the speed of polymerization at the cutoff of UV light increases, approaching the limit, equal to 0.35. This can mean that in the course of light polymerization the long-life active centers, which conduct then after-light process, appear and are accumulated.

Beginning already from small conversions (~3%), molecular weights of obtained polymethyl methacrylate (PMMA) increase with depth of conversion, moreover in course of post-polymerization molecular weights increase more rapidly than during uninterrupted photoinitiation. However, as a whole molecular weights obtained in these tests of PMMA are approximately two orders higher than during the polymerization of MMA in the absence of phosphoric acid. The preliminary analysis of the molecular-weight distributions of the products of polymerization showed that with an increase in the conversion with the post-polymerization the molecular-weight distribution becomes narrow.

Processes of engendering and transforming radicals in system MMA -  $H_3PO_4$  were studied with the aid of method EPR and calorimetry in course of low-temperature post-polymerization, initiated by  $\gamma$ -rays. It was discovered, that with the defrosting of the irradiated system of MMA -  $H_3PO_4$ , higher than temperature of the vitrification of mixture ( $-90^\circ$ ) begins the rapid post-polymerization, initiated by those

accumulated during irradiation by radicals, with which the concentration of macroradicals remains constant, i.e., the death of active centers is absent. Inverse proportionality between molecular weight of the generatrix of polymer and number of radicals must be the kinetic result of this.

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Calculated and experimentally specific molecular weights coincide well, which is the confirmation of radical nature of process.

Experimental data on low-temperature post-polymerization in system MMA -  $H_3PO_4$  correlate well with data on photo-initiated post-polymerization in liquid phase: and in that, and in other case introduction  $H_3PO_4$  leads to practical disappearance of reaction of death of macroradicals with retention/maintaining of capacity to participate in reaction of propagation in chain. The mechanism of this phenomenon can be connected with change in the conformational properties of macroradicals of PMMA and their association as a result of complex formation  $H_3PO_4$ .

It was received by the editorial staff 7 Oct. 1971.

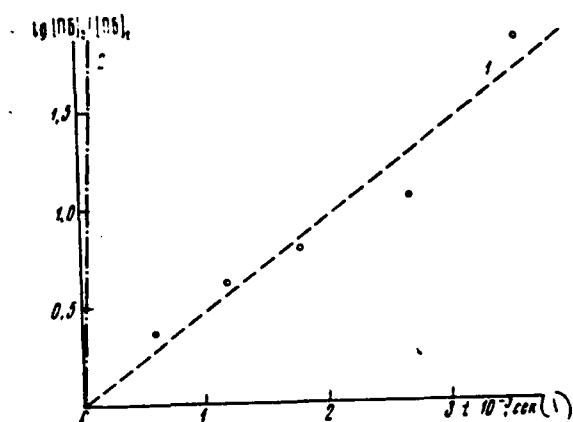
HIGH-PRESSURE EFFECT ON DECAY RATE OF BENZOYL PEROXIDE IN POLYMETHYL METHACRYLATE.

R. Rado, F. Sech.

Dear editor

During heating of peroxide of isobutyryl in isooctane under pressure (50°) acceleration of reaction of its decomposition was observed, moreover approximately up to a pressure of 2000 kgf/cm<sup>2</sup> logarithm of rate constant of decomposition linearly depends on pressure [1].

We revealed/detected that in polymethyl methacrylate (PMMA), which contains 1.8 wt.o/o of benzoyl peroxide (PB), at pressure 10<sup>4</sup> kgf/cm<sup>2</sup> and temperature of 150° inverse effect occurs, i.e., retardation of reaction of decomposition. At the atmospheric pressure the decay rate of PB in PMMA at 150° is so great which experimentally does not succeed in measuring it by usual methods. A semiquantitative evaluation of this retarding high-pressure effect on the decomposition of PB can be carried out by the comparison of the rate constants of decomposition at an identical temperature. The rate constant, determined from the experimental data obtained by us according to the equation for the monomolecular reaction, has a value  $1.1 \pm 0.2 \cdot 10^{-3} \text{ s}^{-1}$ .



Logarithm of the ratio of initial concentration of PB to its concentration after decomposition during  $t$  depending on time at  $150^\circ$  and pressure  $10^4$  kgf/cm $^2$  in the medium of PMMA (1) and at a pressure 1 kgf/cm $^2$  and a temperature of  $80^\circ$  in the medium of benzene (2) [2].

Key: (1). s.

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It is at the same time known that the corresponding kinetic parameter for temperature of  $150^\circ$  and atmospheric pressure in the case of decomposition of PB in the benzene is  $4 \cdot 10^{-2} \text{ s}^{-1}$  [2]. In the figure for the comparison the results obtained by us on the decomposition of PB are given to PMMA at a pressure  $10^4$  kgf/cm $^2$  and literature data of decomposition of PB in the benzene at  $80^\circ$  and the pressure 1 kgf/cm $^2$ , when  $k = 36 \cdot 10^{-3} \text{ s}^{-1}$  and  $E_a = 30 \text{ kcal/mole}$ .

It was received by the editorial staff of 11 Oct. 1971.

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Page 604.

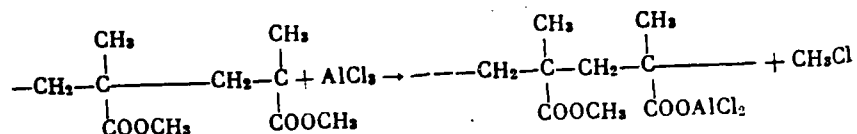
REACTION OF POLYMETHYL METHACRYLATE WITH ALUMINUM CHLORIDE.

A. Ye. Kulikova, L. A. Gershteyn, Ye. N. Zil'berman, T. S. Yastrebova.

During reaction of esters with aluminum chloride aluminum salts of carboxylic acids are formed and halogen-alkanes [1, 2] are separated/liberated. In the present work this reaction is used for the modification of polymer with the lateral ester groups - polymethyl methacrylate (PMMA).

During heating up to  $130^{\circ}$  and thorough mixing of mixture of PMMA and aluminum chloride is observed formation of polymers, which contains aluminum and chlorine, and liberation/precipitation of methyl chloride. In the IR-spectrum of the modified polymer, which contains aluminum (which corresponds to the relationship/ratio of links of MMA and methacrylatedichloridealuminum equal to 10:1) is revealed the new strip in the region  $1630\text{ cm}^{-1}$ , which relates to the salt groups of the type -  $\text{COOMe}^+$ . From the comparison of data of the analysis of polymer, which contains 2.6%  $\text{AlCl}_3$ , it follows that the relationship/ratio in it of aluminum and chlorine composes 1:2 with respect (to 7.5% of chlorine), i.e., in the reaction one atom of chlorine of three in the molecule of aluminum chloride participates. In the cases, when modification is conducted at the smaller depth, this relationship/ratio it is impossible to determine in view of a

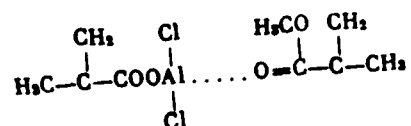
small quantity of chlorine, whose content is located on the face of error in determination. Reaction of PMMA with the aluminum chloride can be represented by the following diagram:



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Analogous reaction is known for esters of unsubstituted lowest acids: ethylacetate reacts with aluminum chloride with replacement only of one atom of chlorine [2].

Obtained polymer only partially is dissolved in common for PMMA organic solvents. According to the data of elementary analysis and IR spectroscopy the soluble fraction is unreacting PMMA. The viscosity of 0.5% solution of this fraction does not differ from the viscosity of initial PMMA. In the undissolved fraction the content of aluminum increases/grows ~3 times. In this case in the IR-spectrum of the undissolved fraction the intensity of the absorption band of salt group ( $1630 \text{ cm}^{-1}$ ) noticeably is increased. The loss of the solubility of modified PMMA, apparently, is caused by intermolecular interaction due to the complex formation between the salt group of one macromolecule and by ester group of another macromolecule [3]

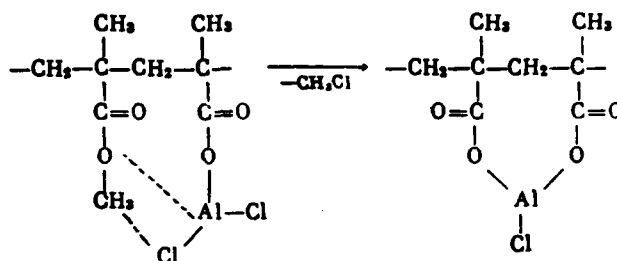




Attention is focused on itself, that with small degree of modification (0.02% of aluminum) completely soluble polymer is obtained.

As it follows from experimental data, temperature of vitrification of modified polymer virtually is not changed with the advent of salt groups. At the same time, the flow point of the modified polymer increases/grows with an increase in the content of aluminum in the polymer, reaching 236° in the presence 0.52% aluminum in the modified polymer. An increase in the flow point of polymer can be explained by the same reasons, which lead to the loss of solubility, i.e., by noted above intermolecular interaction of macro-chains.

We investigated some other properties of modified polymers. It was established that modified PMMA, which contains 0.52% of aluminum, is more heat-stable than initial. So, at 250° in the air flow after 4 hours the degree of the depolymerization of initial PMMA composed 67%, while in modified PMMA under these conditions the degree of depolymerization composed 30%. It is necessary to assume that the depolymerization of PMMA, which as is known, occurs by the radical mechanism, it is retarded, probably, as a result of the formation of internal salt of the type



Presence of such cyclic links impedes depolymerization of modified PMMA with splitting monomer [4]. At 300° thermostability of modified PMMA approached thermostability of initial PMMA.

In composition of pyro-lysate, modified by PMMA, besides monomer, chloride methyl and water were discovered by method of gas-liquid chromatography. The presence in pyro-lysate of methyl chloride can be explained by the reaction of groups - COO - AlCl, with the ester groups of polymer with the formation of groups - (COO), - AlCl and - (COO),Al.

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From modified polymer (0.06% of aluminum) transparent plates were obtained by casting method. The results of tests showed a certain increase in the hardness of material from 10 to 13.8 kg/mm<sup>2</sup>; impact strength of these plates - 12.5 kg·cm/cm<sup>2</sup>. Furthermore, were investigated the electrical properties of the obtained plates. It seemed that the plates of modified PMMA have specific volumetric electrical resistance three orders lower ( $\rho_v = 10^{11} \Omega \cdot \text{cm}$ ), than in initial PMMA ( $\rho_v = 10^{14} \Omega \cdot \text{cm}$ ).

Experimental part.

In work were used freshly prepared aluminum chloride and PMMA, obtained by method of suspension polymerization with specific viscosity 0.5% solution in benzene 0.255.

Content of aluminum in polymer was determined by method of combustion, chlorine in modified polymer - argentometrically after boiling of suspension of polymer in 0.1 n. of solution of sodium hydroxide.

IR-spectrum of products are obtained on double-beam instrument UR-20 with utilization of tablets of KBr.

Thermal breakdown of polymers was conducted in ampule with porous bottom during blowing of air at a rate of 2 ml/min. The products of pyrolysis condensed in the series-connected traps, cooled by the mixture of carbonic acid with acetone.

Chromatographic analysis was realized on instrument "Tsvet-1" with the detector on the heat conductivity, the gas-carrier - helium, the immobile phases: 1) polyethyleneglycoladipate (20%), carrier - Celite-545; 2) Apiezon Z(20%), chromosorb W. The length of column is 1 m, the diameter of 4 mm. Identification was conducted through the time of output/yield and by the method of the introduction of the additives of pure/clean compounds with utilization of both immobile phases. Temperature in thermostat 100°, in rectifier 150°, the speed

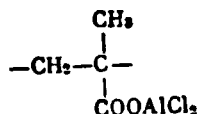
of helium 50 ml/min.

Hardness of casting samples was determined according to GOST 4670-62. Impact number of casting samples was determined according to GOST 4647-62.

For obtaining PMMA with 2.6% of aluminum into double-neck flask/bulb, equipped with mechanical agitator, reflux condenser, connected with trap, cooled by mixture of carbonic acid and acetone, were placed 100 g of PMMA and 21.65 g of aluminum chloride. During 30 min the mixture energetically was mixed at room temperature, and then during 2 hours at 130°. They washed the cooled reaction mass in acidified water before the disappearance of aluminum ions in the wash waters (according to the qualitative reaction on  $Al^{3+}$ ), and then in methanol and dried at 80° in the vacuum to the fixed weight. Output/yield of polymer 99 g. For obtaining PMMA of the smaller degree of modification the suspension of aluminum chloride was less, other conditions of reaction retained by the same.

#### Conclusions/derivations.

Reaction of polymethyl methacrylate with aluminum chloride is studied and it is shown that at elevated temperatures reaction with formation of polymers, which contains links of methacrylatedichloridealuminum



occurs. The obtained polymer possesses the increased thermostability and hardness in comparison with the initial polymer and lowered/reduced specific volumetric electrical resistance.

It was received by the editorial staff of 21 DEC. 1970.

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Page 611.

SPECIAL FEATURES OF THE RELAXATION PROPERTIES OF POLYMERS OF DIFFERENT CLASSES.

Yu. V. Zelenev.

During the study of interrelation of structure of polymers and their properties totality of different physical methods is commonly used that possibility of obtaining mutually complementing information [1] gives. It is expedient to represent the results of the parallel investigation of relaxation phenomena in the polymers by different physical methods in dual correlation diagrams [2] of form:

$$\lg v_{\text{NMR}} - 1/T, \lg v_c - 1/T, \lg \tau_s - T,$$

where  $v_c$  - frequency of correlation of NMR,  $\tau_s$  - most probable relaxation time.

For majority of polymers, which differ in flexibility of chains (rubberlike, solid amorphous and crystalline, and also rigid-chain polymers), manifestation of one segmental and one (or two) local of relaxation processes is characteristic. In this case for the segmental process is characteristic the family of the points, which are stacked to the curve, and for the local - to straight line.

Page 612.

The curvature of dependence  $\lg v_{\text{NMR}} = f(1/T)$  for the process of segmental movement is connected with its cooperative nature and dependence of

the activation energy on temperature [3]. One should note that the construction of correlation diagrams according to separate literature data (as a rule, that contain the results of the analysis of the polymer of a defined class by one or two methods) it leads to the essential scatter of points relative to the appropriate locus (curved or straight line), which is connected with differences in the objects similar on the name, different methods and conditions for measurements. Taking into account this, we carried out the studies of the temperature dependences of mechanical and dielectric losses, time of spin-lattice relaxation  $T_1$ , intensity of radio-thermoluminescence (RTL) and change in the volume for the polymers, which relate to different classes of high-molecular compounds. In this case together with the one-component polymeric systems (natural rubber, polymethyl methacrylate (PMMA), polypropylene (PP) and cellulose) were investigated two-component polymeric systems (statistical ethylene-propylene and divinyl-isoprene copolymers, and also the homogeneous mechanical mixtures of acrylonitrile rubber SKN-18 + SKN-40 and divinyl SKD and butadien SKB of natural rubbers in ratio 1:1). In the region of transition from highly elastic to glassy strained condition D polymers undergoes abrupt change, and the factor of mechanical loss  $\kappa$  passes through the maximum, which is developed in crosslinked-liquid state, which with an increase in the frequency is displaced in the direction of high temperatures. Although the process of vitrification occurs in the specific temperature range, the conventional temperature of transition, called the temperature of mechanical vitrification  $T_{mec}$  is introduced. It can be determined by

continuing the straight portion of dependence  $D = f(T)$  before the intersection with the axis of temperatures. Since this method is to a considerable extent subjective, we proposed [4] to determine  $T_{\text{max}}$  on the mechanical loss maximum, omitting from the apex/vertex of maximum perpendicular to the axis of temperatures. The position of the region of transition depends on molecular weight  $M$  (in view of the tip effect of the molecules on the value of the molecular coefficient of friction) only when  $M < 10000$ . The study of effect of the type of polymer on the relaxation properties of the weakly-structured natural rubbers, which have the approximately identical denseness of three-dimensional/space grid ( $E_c \approx 10 \text{ kgf/cm}^2$ ) showed that the character of their molecular structure plays important role. With the decrease of the regularity of structure and flexibility of the molecular chains of natural rubbers the mechanical loss maxima are increased, are expanded and are shifted/sheared in the direction of high temperatures. For the natural (NK) and synthetic (SKI) isoprene natural rubbers, which have pliable, regular structure the molecular chains, maximums are developed at noticeably lower temperatures and have small height. The decrease of the flexibility of the molecular chains in the natural rubbers SKB and SKS due to the appearance of the asymmetric arranged/located vinyl and phenyl lateral extra weights leads to considerable increase  $T_{\text{max}}$  and  $\chi_{\text{max}}$ . The increase of intermolecular interaction in proportion to an increase in the content of nitrile of acrylic acid (increase in the concentration of polar cyanic groups) in the natural rubbers SKN-18, 26, 40 leads to an even greater shift of maximums in the direction of high temperatures and an



increase in their height.

Dipole-segmental dielectric losses in vulcanizates of natural rubbers depend on quantity of polar sulfur bridges, since during vulcanization each atom of sulfur, being joined with two atoms of carbon, is polarized under effect/action of atoms of carbon and hydrogen, forming permanent dipole moment. In the electric field the orientation of the dipoles, which accomplish rotational oscillations/vibrations, occurs under the effect of the thermal agitation, to which contributes an increase in the mobility of macro-chains upon transfer into the highly elastic state.

Page 613.

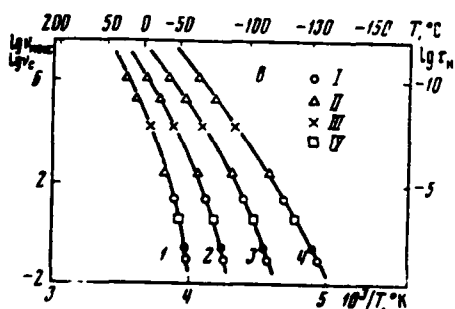
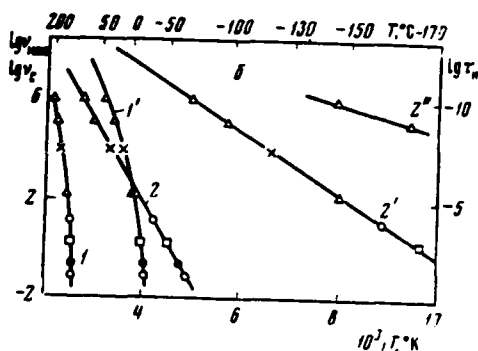
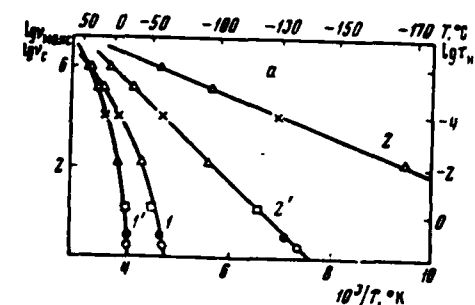
During the study of the dielectric properties of polar natural rubbers (SKN-18, 26, 40) and their sulfuric vulcanizates in the range of temperatures of  $-180-100^{\circ}$  were discovered maximums  $\text{tg}\delta$  both when  $T > T_c$  and when  $T < T_c$ .

In region of transition from highly elastic to glassy state for natural rubbers of different structure (NK, SKS-30, and SKN-40) line broadening of NMR is observed. When a change in the molecular mobility did not affect the value of the width of line  $\Delta H$ , the values of second moment  $\Delta H^2$ , which make it possible to produce the comparison of experimental data with the theoretical for the cases of rigid structure and moving the separate molecular groups [5] were computed. The character of temperature dependences  $\Delta H^2$  testifies about the

presence of the sharper boundaries of the region of the manifestation of this transition, which has a value during the estimation of the energy of the activation of this process. The comparison of the temperature intervals of this transition and regions of relaxation, which are developed in the mechanical and electric fields, makes it possible to consider that it is also connected with a change in the segmental mobility. The removal/taking dependences  $\Delta H = f(T)$  for the natural rubbers, which contain and which do not contain group  $\text{CH}_2$ , showed that also with further temperature decrease is continued the monotonic line broadening of NMR. It is less expressed for the regular isoprene natural rubbers NK and SKI and is more noticeable in the case of irregular atactic natural rubbers SKB, SKS and SKN, which is caused by a difference in their free space. Comparison of these results with the measurement data in the mechanical and electric fields makes it possible to assume that the line broadening of NMR continuous with a temperature decrease (differing for the different natural rubbers) is caused not only by the residual mobility of the methyl groups  $\text{CH}_3$ , but also by the mobility of the methylene groups  $\text{CH}_2$ , which are contained in the main chains of all natural rubbers being investigated.

Study of RTL of polymers of different structure showed that by removing/taking temperature dependences of luminous intensity  $I$ , it is possible to obtain useful information about relaxation transitions and special features of structure of polymers. In samples of one and the same polymer curved luminescences essentially differ from each other,

if they are distinguished by the concentration of molecular bonds or by the degree of crystallinity [6].



Dual correlation diagrams for the segmental (1, 1') and local (2-2'') processes of the block polymers of the different structure: a) NK (1, 2); ETs (1', 2'); b) PMMA (1, 2, 2'); PP (1', 2''); c) for random copolymers (1, 4) and the homogeneous mixtures of polymers (2, 3); I - data of mechanical, II - dielectric measurements, III - NMR, IV - TRL, black points - dilatometry.

The dependence of the position of maximums on the speed of warm-up is the proof of the existence of the bond between the position of peaks in the curve of luminescence and the temperature of structural transitions. An increase in the speed of warm-up leads to the fact that the maximums in curve  $I=f(T)$  are shifted in the direction of high temperatures, without changing its form. For the polymers of different structure the position of maximum in the curve of luminescence  $T_{max}$  and the speed of warm-up  $w$  are interlocked:

$$1/T_{max} = C_1 - C_2 \lg w.$$

Comparison of data, obtained by different methods, makes it possible to make substantiated reference of developed processes to appropriate forms of mobility. On the figure, a the correlation dependences of segmental and local processes for sulfuric vulcanizate NK and ethylcellulose are given. Local mobility in the NK is caused by the lateral extra weights (methyl groups  $CH_3$ ) and with the adjacent them methylene groups  $CH_2$  of the main chain. For ethylcellulose the local relaxation process, caused by the mobility of  $CH_2OH$ -groups in its disordered regions, also distinctly is developed. On the figure, b are given analogous dependences for amorphous PMMA, which has both the lateral extra weights (groups  $CH_3$ ), and bulky lateral methylether/ester groups, and for the partially crystalline PP. For PMMA the existence of two forms of local mobility with the different temperature coefficients of relaxation time  $\tau$  is characteristic. The local process of relaxation in PP is connected with the mobility of  $CH_2$ -groups. As follows from the figure, c, for the random copolymers

of ethylene and propylene, divinyl and isoprene, and also for the uniform mechanical mixtures of acrylonitrile rubber SKN-18+SKN-40 and natural rubbers SKD+SKB is developed one main region of relaxation, connected with the segmental mobility (to it it corresponds as in the case of one-component polymeric systems, the bent correlation dependence). One should note that not all forms of local processes can be fixed by all five physical methods, whereas for the segmental processes all applied methods prove to be sufficiently sensitive.

#### Conclusions/derivations.

Is examined character of course of relaxation processes in flexible-chain, semirigid-chain and rigid-chain polymers, and also in copolymers and mechanical mixtures of polymers. Are analyzed the special features of local and segmental processes in the polymers of different classes according to the data of their study by different physical methods of relaxation spectrometry.

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